Si/BDD/TiO_2 Anodes: Morphology and Efficiency For the (Photo)Oxidation of Oxalic Anions

O. Enea
UMR CNRS C 6503, University of Poitiers, 86022 Poitiers, France

B. Correa
IGC, Swiss Federal Institute of Technology, Lausanne, Switzerland

A. Perret, W. Haenni
CSEM, Swiss Centre of Electronics and Microtechnics, Neuchâtel, Switzerland
werner.haenni@csem.ch

Large area, up to 0.3 m^2 , conducting diamond films, can be now deposited on various substrates such as metallic foils, ceramics or silicon wafers [1]. Nevertheless, the electrically conducting boron doped diamond (BDD) films possessing outstanding mechanical, thermal and chemical qualities, have never been used as substrates for TiO_2 deposits conducting to a wide range of (photo)electrochemical applications. However, TiO_2 layers deposited on various substrates such as conducting glasses [2], titanium foils [3] or glass fibers [4] have been recently used in applications such as solar cells [1] or solar decontamination of water [3], [4].

In order to reach more fundamental information about the morphological and photo-electrochemical properties of TiO_2 layers deposited onto conductive boron doped diamond (BDD) films one micron thick, we have systematically studied several thin layers of TiO_2 having thickness between 100 nm and 10 μm. These films have been prepared either from colloidal suspensions of TiO_2 (30g/L) in methanol [2] or from 11% wt. TiO_2 aqueous suspensions [1], followed by their drying at 200 °C and cooking at 450 °C for one hour. The thickness of TiO_2 layers deposited on Si/BDD small sheets has been measured with a Tenchor profilometer. Their morphology, examined with an AFM (Nanoscope III) microscope working in the tapping mode, has evidenced large clusters of 90 - 110 nm in diameter, made of smaller (25 - 35 nm) TiO_2 particles. The plateau photocurrents and onset potentials of all Si/BDD/TiO_2 samples have been evaluated from the I-E profiles recorded under chopped light. The maximum photocurrent values (0.25 $mA.cm^{-2}$) are smaller (50% less) than those reached for nano-crystalline Ti/TiO_2 photoanodes but good enough for many (photo) electrochemical applications. We have thus used such TiO_2 layers deposited onto a Si/BDD electrode 100 mm in diameter for the (photo)electrochemical decontamination of water in a flow, bipolar cell. The results obtained during the long term experiments carried out for the abatement of 1M oxalic acid in 1M $HClO_4$ show a current efficiency close to 100% in the case of Si/BDD/TiO_2 electrodes, while only 70% can be reached for a Si/BDD electrode without TiO_2 deposits. Moreover, under UV irradiation, the photo-produced holes at the surface of TiO_2 layers can significantly improve the current efficiency, which quickly decreases as soon as the concentration of oxalic ions becomes too low.

References

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